The Promotional Effect of Initiators in Hydro-thermal Cracking of Resids

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1 Introduction

Based on cracking mechanism, there are three main industrial processes to produce middle distillate from resid.   They are thermal cracking, catalytic cracking and hydrocracking. Hydro-thermal cracking, the combination of thermal cracking and catalytic hydrogenation, is a novel method developed by the present authors to upgrade resids aiming at maximum middle distillate (Fujimoto et al., 1988; Yang et al., 1998).   The following elementary steps are important during hydro-thermal cracking reactions: (1) Initiation free radical (homolytic cleavage of a hydrocarbon molecule into two free radicals).   (2) Free radical dissociation (β scission).   (3) Hydrogen transfer (between H_2, radical and hydrocarbon).   H transfer from H_2 to radical can suppress the secondary cracking of hydrocarbon, therefore, suppress the yields of coke and gas.   It is considered that some effective initiators may enhance the conversion of resids by increasing the concentration of free radicals.   Much research has been carried out on catalyst development, reaction mechanism, process design and optimization in the above refinery processes until now.   But the issue of adding initiators in the cracking of resids was very rarely addressed.   The present work shows the promotional effect of initiators in hydro-thermal cracking of resids as well as its model compound.

2 Experimental

Experiments were carried out in a 75 cm³ batch reactor.   The reaction conditions were as follows: temperature, 673-703K; initial pressure, 5.0 MPa; reaction time, 0-60 min; catalyst/oil ratio, 0.05-0.2.   Canadian bitumen (B) and Arabian heavy vacuum resid (AVR) were used in experiments.   Their properties are shown in Table 1.

Sulfur and $(CH_3)_3COOC(CH_3)_3$ (DTBP) were used here as initiators to promote heavy oil conversion.

Gas products were analyzed by gas chromatography (Shimadzu GC-8A).   Liquid products were separated by a distillation gas chromatography (Shimadzu GC-14A) into 5 components: naphtha (initial boiling point –343K), kerosene (343-503K), gas oil (503-616K), vacuum gas oil (616-798K) and residue (>798K).   The conversion of resid was calculated by the following formula:

$$\text{Conversion (wt\%)} = (1 - \frac{\text{residue in product}}{\text{residue in feed}}) \times 100\% .$$

When alkylbenzene was pyrolyzed or cracked on solid acid catalyst, the selectivities of benzene and toluene were so different that it could be used as a model compound to distinguish a reaction proceeding via carbonium mechanism or free radical mechanism (Szware 1950; Mochida and Yoneda 1967; Nakamura et al, 1997).   Study on liquid-phase thermolysis of 1-phenyldodecane (PhDD) demonstrated that PhDD pyrolysis entirely proceeded through free radical mechanism (Savage and Klein, 1987).   The reaction of PhDD was used as a probe reaction to study the mechanism of initiator promotional effect.   In these experiments, the liquid products were determined by GC-MS (Shimadzu GCMS 1600) and analyzed by gas chromatography (Shimadzu GC-14A).

3 Results and Discussion

3.1 Effect of initiators addition in resids

1 wt% of DTBP was added into bitumen to study the effect of initiator.   The properties of products are listed in Table 2.   It was obvious that this peroxide was very effective to increase the conversion of bitumen from 59.1% to 91.9% (runs 1 and 2 without catalyst) and from 68.4% to 78.5% (runs 3 and 4 with catalyst) respectively.   Coke yield was greatly suppressed by catalyst (runs 3 and 4).

It also was seen from Table 2 that in the cases of adding DTBP, the selectivity of iso-butane was higher than that without DTBP. It is well known that thermal cracking of hydrocarbon molecule proceeded via the chain reaction of free radicals generated from C-C cleavage or hydrogen atom abstraction from C-H bond. In bitumen hydro-thermal cracking, free radicals were generated from C-C cleavage at initial stage. But when DTBP was added into bitumen, it decomposed at high temperature and produced tertiary butoxy radical. This free radical could abstract hydrogen from bitumen and initialized chain reactions at initial stage besides the conventional initiation path, therefore the concentration of radical was higher and the conversion of bitumen was increased.

3 wt% of sulfur was added into AVR to test the effect of initiator addition. The results were compared in Table 3. When catalysts were used, the addition of sulfur increased the conversion from 63.6% to 81.1% (runs 5 and 6). In absence of catalyst, the addition of sulfur raised the conversion from 15.7% to 32.5% (runs 7 and 8). Similarly, sulfur was an effective initiator to the hydro-thermal cracking of AVR.

3.2 Study on model compound

The conversions in different case at different reaction time are depicted in Fig.1. It is clear from Fig.1 that the conversion was obviously enhanced by adding initiator with or without catalyst. Without catalyst and with initiator, when the reaction time was one hour, the conversion increased from 40.1% to 51.9%. In absence of initiator, catalyst greatly decreased the conversion from 40.1% to 16.8% in one-hour reaction. It seemed that free radicals were hydro-quenched over catalyst. After adding initiator to catalyzed reaction, the conversion restored to 40.2% even if the reaction time was just half of an hour. If the reaction time was extended to one hour, the conversion of the catalyzed reaction with addition of peroxide was further enhanced to 47.5%. The selectivities of part products are shown in Table 4. It was found from Table 4 that the ratios of toluene to benzene were about 18.0-22.2 in all of these cases. This indicated that hydro-thermal cracking of PhDD proceeded via free radical mechanism and hydrogenation quench. In the cases of adding peroxide, iso-butene, acetone and tertiary butyl alcohol were detected in products and selectivity of C_1 species was also increased. In run 11, the feed was heated from room temperature to 683K in 10 min and cooled down immediately, to 573K in 5 min and to room temperature in another 15 min (reaction time = 0). The yield of acetone was high. It should be derived from decomposition of tertiary butoxy radical, with the corresponding formation of C_1 species (Fan et al., 1998). This provided the evidence that the decomposition of DTBP was the initial stage of the chain reactions.

The above results suggested that the hydro-thermal cracking of PhDD related with free radical chain reactions. It was considered that in the chain reactions, the initiation step of PhDD molecule dissociation, forming free radicals, was the slowest one, the overall reaction rate was readily controlled by this step. If the concentration of free radicals in reactants was increased, the reaction rate could be elevated. When DTBP was added into PhDD, it easily produced free radicals during hydro-thermal cracking conditions, therefore increased the overall concentration of free radicals, enhanced the conversion of PhDD. If effective free radical initiators are available, the conversion of resid in hydro-thermal cracking, thermal cracking or hydrocracking will be raised and the reaction temperature may be lowered. The experiments showed that DTBT and sulfur are effective promoters to resid conversion.

4 Conclusions

DTBP remarkably enhanced the conversion of resid and its model compound during hydro-thermal cracking. This resulted from tertiary butoxy free radical produced by the decomposition of peroxide at reaction condition. Similarly, sulfur was an effective promoter to the hydro-thermal cracking of AVR.

5 References

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Table 1 Properties of feedstock

	B	AVR
API Gravity	6.0	5.9
CCR, wt%	14.8	22.4
C, wt%	82.89	84.80
H, wt%	10.14	10.20
S, wt%	4.90	4.02
Ni, wtppm	75	53
V, wtppm	192	180
Naphtha, wt%	0	0
Kerosene, wt%	0	0
Gas oil, wt%	6.8	0
VGO, wt%	28.0	0
Residue, wt%	65.2	100.0

Table 2 Effect of DTBP addition on hydro-thermal cracking of bitumen

Run number	1	2	3	4
Catalyst	no	no	Ni/Al_2O_3	Ni/Al_2O_3
DTBP	no	adding	no	adding
Conversion, %	59.1	91.9	68.4	78.5
yield, wt%				
C_1-C_4	4.3	5.4	4.2	5.0
iC_4H_{10}/nC_4H_{10}	0.50	0.84	0.50	1.46
Naphtha	9.1	12.4	7.4	9.6
Kerosene	9.4	11.9	8.0	9.1
Gas oil	22.6	28.4	22.7	25.0
Vacuum gas oil	21.8	29.9	31.8	32.3
Residue	26.7	5.3	20.6	14.0
Coke	4.6	5.1	3.0	2.8

Temperature 703K, pressure 5.0MPa, Bitumen 10.00g, catalyst 2.00g , DTBP 0.10g

Table 3 Effect of sulfur addition on hydro-thermal cracking of AVR

Run number	5	6	7	8
Catalyst	$NiMo/Al_2O_3$	$NiMo/Al_2O_3$	no	no
Initiator	no	0.3g S	no	0.3g S
Time, min.	60	60	0	0
Conversion, %	63.6	81.1	15.7	32.5
yield, wt%				
C_1-C_4	3.3	4.9	0.1	0.1
Naphtha	4.8	9.2	0.2	1.1
Kerosene	6.1	9.7	0.5	1.4
Gas oil	16.5	21.6	2.3	6.3
Vacuum gas oil	28.6	27.8	12.7	23.6
Residue	34.5	18.8	84.3	67.6
Coke	3.2	6.4	-	-

Temperature 703K, pressure 5.0MPa, AVR 10.00g, catalyst 2.00g

Table 4 Effect of DTBP addition on model compound

Run number	9	10	11	12
Conversion, %	40.1	51.9	19.5	47.5
Selectivity, %				
acetone	0.0	2.86	9.83	0.0
t-butyl alcohol	0.0	0.0	1.56	0.0
n-olefin C_5-C_8	3.03	3.22	0.63	0.0
n-paraffin C_5-C_8	5.76	6.69	0.75	7.03
n-olefin C_9-C_{13}	18.8	7.62	13.8	4.36
n-paraffin C_9-C_{13}	22.2	24.4	15.8	33.9
toluene / benzene	21.3	22.2	18.0	19.2

Temperature 683K, pressure: 5.0MPa

Run 9:　reaction time 60 min. no catalyst and no peroxide

Run 10:　reaction time 60 min. adding 0.40g peroxide only

Run 11:　reaction time 0 min. adding 0.40g peroxide only

Run 12:　reaction time 60 min. adding 0.40g peroxide and 0.50g catalyst
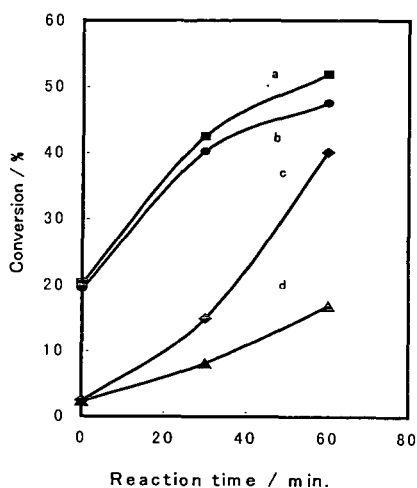

Fig.1 Effect of DTBP on conversion of PhDD

　　　Feed: PhDD 10.00g, temperature 683K

　　　pressure 5.0MPa

　　　a: adding 0.40g DTBP only

　　　b: adding 0.40g DTBP and 0.50g catalyst

　　　c: no DTBP and catalyst

　　　d: adding 0.50g catalyst only